

**INVESTIGATION OF ELECTROCHEMISTRY
OF
HIGH ENERGY COMPOUNDS IN ORGANIC ELECTROLYTES
THIRD PROGRESS REPORT**

November 1, 1965 to April 30, 1966

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R. T. Foley, L. E. Helgen, and L. Schubert

Prepared for the
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Table of Contents

	Page
Abstract	
I. Scope	1
II. Chemical Stability of Cyclic Esters	3
A. Reaction with Metals (Na, K, Li, Ca, Mg) . . .	3
Experimental	3
Results	4
Discussion	5
B. Reaction with Chlorine	9
III. Range of Electrolysis	12
A. General	12
B. Solvent Characterization	12
C. Reference Electrode	22
IV. Conclusions and Direction of future effort	29
V. References	31

Abstract

This phase of the investigation has been concerned with the chemical and electrochemical properties of the cyclic esters, gamma-butyrolactone and propylene carbonate. The reactions of these esters with the metals Na, K, Li, Ca, and Mg have been studied. Reaction of butyrolactone with Na indicates that both condensation and ring opening with the formation of the sodium salt of a hydroxy carboxylic acid occurs along with the evolution of hydrogen. Chlorine reacts with propylene carbonate both at room temperature and at 100°C to yield a chemical species that absorbs in the UV.

Work has continued on the range of electrolysis of the cyclic esters particularly in connection with establishing a suitable reference electrode. The stability of the silver reference electrode was measured. On the basis of experimental evidence as well as literature reports it was concluded that the silver-silver ion reference was most suitable for the non-aqueous systems under investigation here.

I. SCOPE

This investigation deals with the electrochemistry of high energy compounds in organic electrolytes, "high energy" referring to those elements or compounds that can be used in electrochemical cells to convert chemical to electrical energy. In previous reports (1, 2) it was pointed out that a considerable amount of basic information on the electrochemical (and chemical) properties of organic solvents was lacking. In particular, it was not known precisely over what ranges electrolytic solutions could be electrolyzed without solvent decomposition occurring. This "range of electrolysis" for the electrolytic solution is, of course, the maximum range over which the solution can function as the electrolyte of a battery. The ranges of electrolysis of a number of solutions of various solutes in propylene carbonate, gamma-butyrolactone, and gamma-valerolactone were measured and found to be in the 5-6 volt range. It was recognized that the accurate measurement of the cathodic or anodic limiting potential depended on the potential of the reference electrode and it was indicated that this was a problem requiring further study. The second area of investigation has to do with the chemical stability of the solvents in the presence of Na, K, Li, Ca, and Mg, which metals might be used either as anode materials or in salt form in supporting electrolytes, the cation of which might be electrodeposited. Observations and measurements on both of these areas are reported in this progress report.

As mentioned previously the general objective of this work is to establish the principles that will be useful in achieving an understanding of the mechanism by which the solvents and the electro-active materials operate in these high energy electrochemical systems.

II. CHEMICAL STABILITY OF CYCLIC ESTERS

A. Reaction with Metals (Na, K, Li, Ca, Mg)

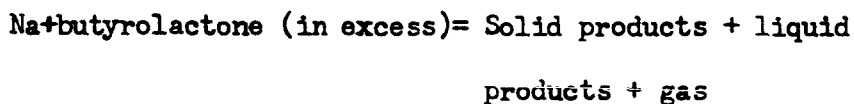
Experimental

A description of the experimental procedure used to study the reactions of Li, K, Na, Ca, and Mg with butyrolactone and propylene carbonate was given in the previous report (2). The weighed cleaned metals were held at 100°C in the redistilled solvents for 100 hours with dried nitrogen gas being passed over the reaction mixture. Following the reaction, the mixture was cooled to room temperature and the components separated and reweighed. The solid, liquid, and gaseous products were analyzed. Several techniques were utilized in the identification and analysis. For mixtures of liquids the gas chromatograph was used. The instrument was a Nester/Faust Anakro instrument with a diethylene glycol succinate column operating under the following conditions: column temperature, 125°C; preheat temperature, 145°C; flow rate of helium gas through column, 60 cc/min; reference flow rate, 54cc/min; size of sample injected, 50 µl. This column has been capable of separating butyrolactone and its decomposition products. This is discussed below under solvent characterization.

For the identification of certain unknown compounds and derivatives infrared absorption was employed. The instrument used was a Beckman model IR-8. Ultraviolet and visible spectra were studied with a Beckman model DB-G. Thin layer chromatography was also successfully used in separating mixtures of unknowns. The absorbent was a silica gel G-zinc silicate mixture. The slurry for coating the glass slides was composed of 30 g. silica gel G, 0.25 g. ZnSiO_3 and 60 ml. H_2O .

Results

The reaction between Na and butyrolactone has been given the most attention recently. Schematically, the observations made on this reaction may be summarized in the following way:



Certain statements can be made with regard to the liquid products. This refers to the compounds which remain in the solvent following reaction. At least three compounds were found to be present after the reaction in addition to the butyrolactone. These were low boiling compounds which could be separated with the gas chromatograph and constituted about 1% of the solution. Chemical identification tests suggested compounds with functional groups including unsaturated groups and alcoholic OH, but the existence of carbonyl structures other than that occurring in esters was doubtful.

The solid product comprises the greater part of the product on a weight basis. For example, on the average of four experiments in which 0.75 g. of Na was reacted, 4.93 g of this material was produced. On the basis of the weight gained and the atomic weight of sodium the molecular weight of the compound was calculated as 151 (± 10). This compound had a melting point range of 132-136°C indicating some contamination. The infrared spectra gave reasonable agreement with the spectra for the sodium salt of γ -hydroxy butyric acid. The comparison compound was synthesized by heating 50g. of γ -butyrolactone, 23 ml. of ethanol, 5 ml. of water, and 22 g. of NaOH under reflux for 30 minutes. The salt was recrystallized with ethanol. The molecular weight of the sodium salt of hydroxy butyric acid is

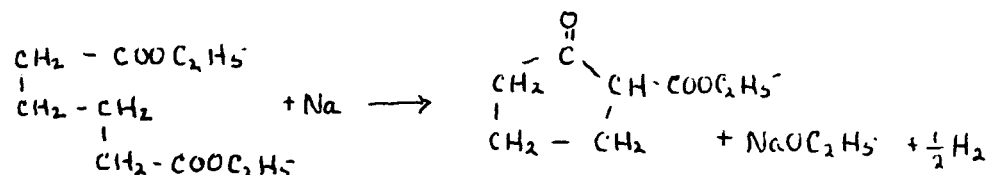
calculated as 126, approximately in agreement with the above figure considering experimental error. Ethanol solutions of the solid product were spotted on the thin layer chromatographic plate and separated into five spots. Only one of these was identified as the sodium salt of a hydroxy carboxylic acid. It is obvious that the solid product contains a number of individual compounds but it appears that the major reaction was one of ring opening and the formation of the sodium salt of the hydroxy acid.

In the experiments described above dry nitrogen was passed over the reaction mixture during the 100-hour experiment. In a similar type of experiment in a closed system the gas evolved when 0.20 g. of Na was reacted with 20 g. of butyrolactone was measured. Gas was evolved continually for 20 minutes at which time it appeared that the sodium metal was all reacted. The amount of gas produced was 60.8 ml. Qualitatively this gas appears to be hydrogen, i.e. there was no precipitate when the gas was bubbled through calcium hydroxide solution, and the gas exploded when ignited. For this amount of hydrogen to be produced by water in the butyrolactone a water content of 0.79% would be required. This amount can be detected by the gas chromatograph as discussed below but was not seen in the chromatograms of the solvent used in the experiment.

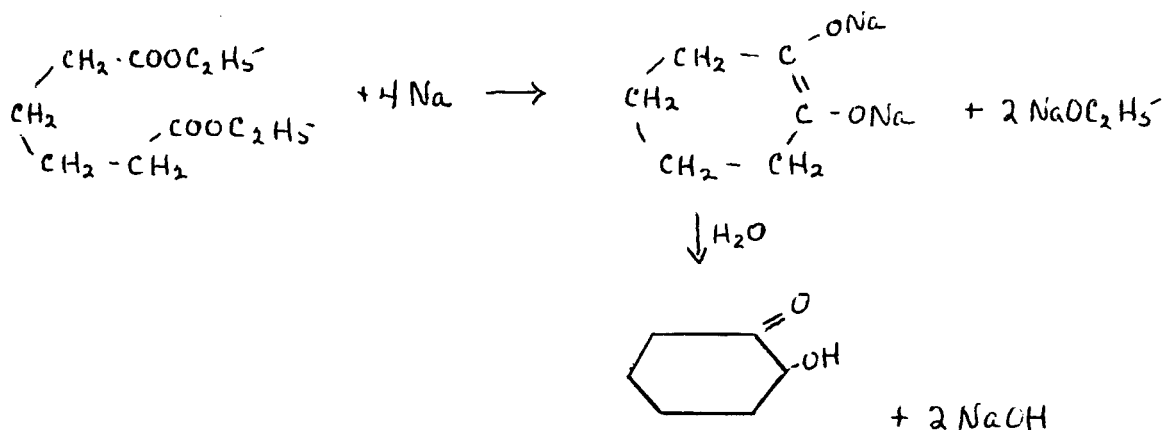
Discussion

There are at least two fundamentally different kinds of reactions known to occur when esters and sodium metal are heated together. Condensation reactions, illustrated below by a Dieckmann condensation,

involve intermediate formation of a sodio derivative and will be accompanied by the evolution of hydrogen gas (14).



The other basic type of reaction is the acyloin condensation which requires four moles of sodium, produces no gaseous by-products, and gives a very different type of product (15).

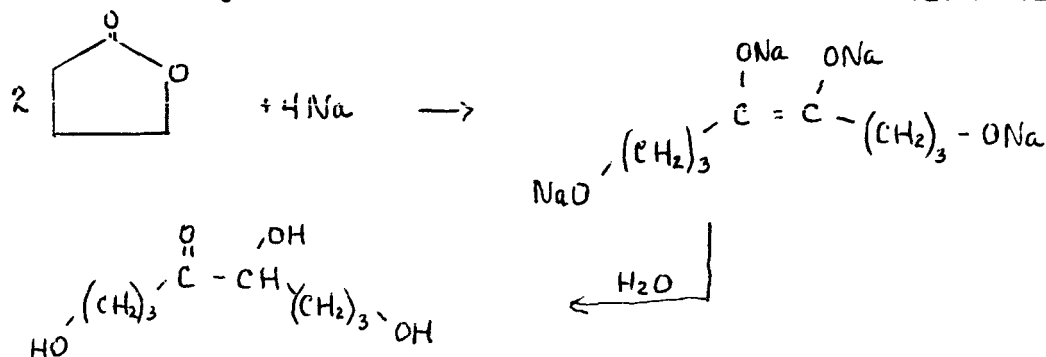


Both of these reactions produce sodium alkoxides as by-products which must be expected to catalyze further reactions.

These facts can serve as starting points for understanding the analogous reactions in the present investigation. Both sodium and potassium have been found to react with butyrolactone and with propylene carbonate. The butyrolactone-sodium reaction proceeds with evolution of a gas. Qualitative tests (limewater and combustion) suggest that hydrogen is the only gaseous product and a semi-quantitative determination of the amount evolved leads to the conclusion that 63% of the sodium added leads to reactions accompanied by hydrogen evolution. The remaining 37% must then be

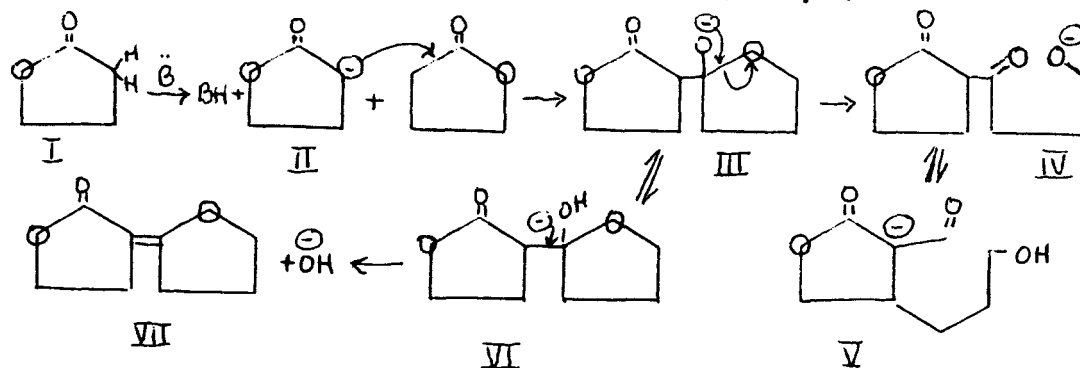
involved in acyloin-type reactions where butyrolactone, or some reactive intermediate is reduced without hydrogen production.

The acyloin-type product to be expected from the reaction of two moles of butyrolactone and four moles of sodium is indicated below.



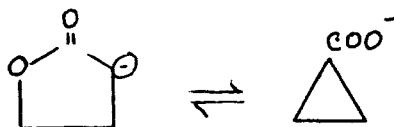
It is of interest that the tetrasodio intermediate is itself a strong base and could serve to catalyze condensation reactions of butyrolactone by removing an acidic α -hydrogen.

The first step in the condensation type reactions is removal of an α -hydrogen by any of the possible bases in the reaction mixture. One possibility for the resulting anion is analogous to the Claisen condensation and is outlined below (I \longrightarrow V).

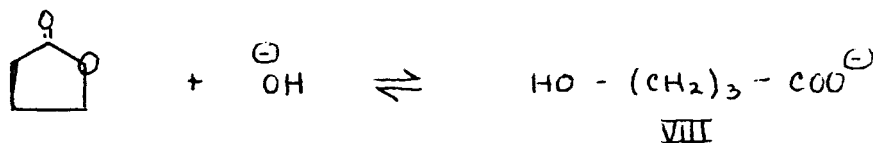


An interesting variation I \longrightarrow VII has been observed when butyrolactone was treated with alcoholic sodium ethoxide (16). There are, of course, any number of further possible condensation reactions as

well as the formally allowable isomerization below.



The reaction that produces VII above also gives rise to hydroxide ion. This makes possible the base catalyzed ring opening reaction that takes place so rapidly in aqueous base.



Experimentally there is encouraging support for this view of the manner in which butyrolactone and sodium react. The products observed include the hydrogen gas mentioned previously, small amounts of three low-boiling liquids, and a mixture of at least five solid products insoluble in butyrolactone. One of these solids has been separated by thin layer chromatography and shown to be the sodium salt of γ -hydroxybutyric acid by independent synthesis. This requires hydroxide ion which in turn requires a dehydration step which suggests that VII will prove to be a component of the mixture of products. The potential mechanistic complexities of the reaction suggest a richness of products which is indeed confirmed by analysis of the reaction mixture.

B. Reaction with Chlorine

The stability of propylene carbonate and of butyrolactone in the presence of the halogens is of interest aside from general considerations of chemical reactivity. The employment of AgCl , CuF_2 , (3, 4) and similar compounds as cathode materials, the use of halides to furnish conducting solutes (5), the chlorination of $\text{AlCl}_3 + \text{LiCl}$ solutions (6) to improve their stability, make possible the production of the free halogen in the solution.

It is mentioned in the literature (7) that chlorine reacts with butyrolactone at 140°C to yield alpha-chlorobutyrolactone. Reaction rates at lower temperatures are not cited.

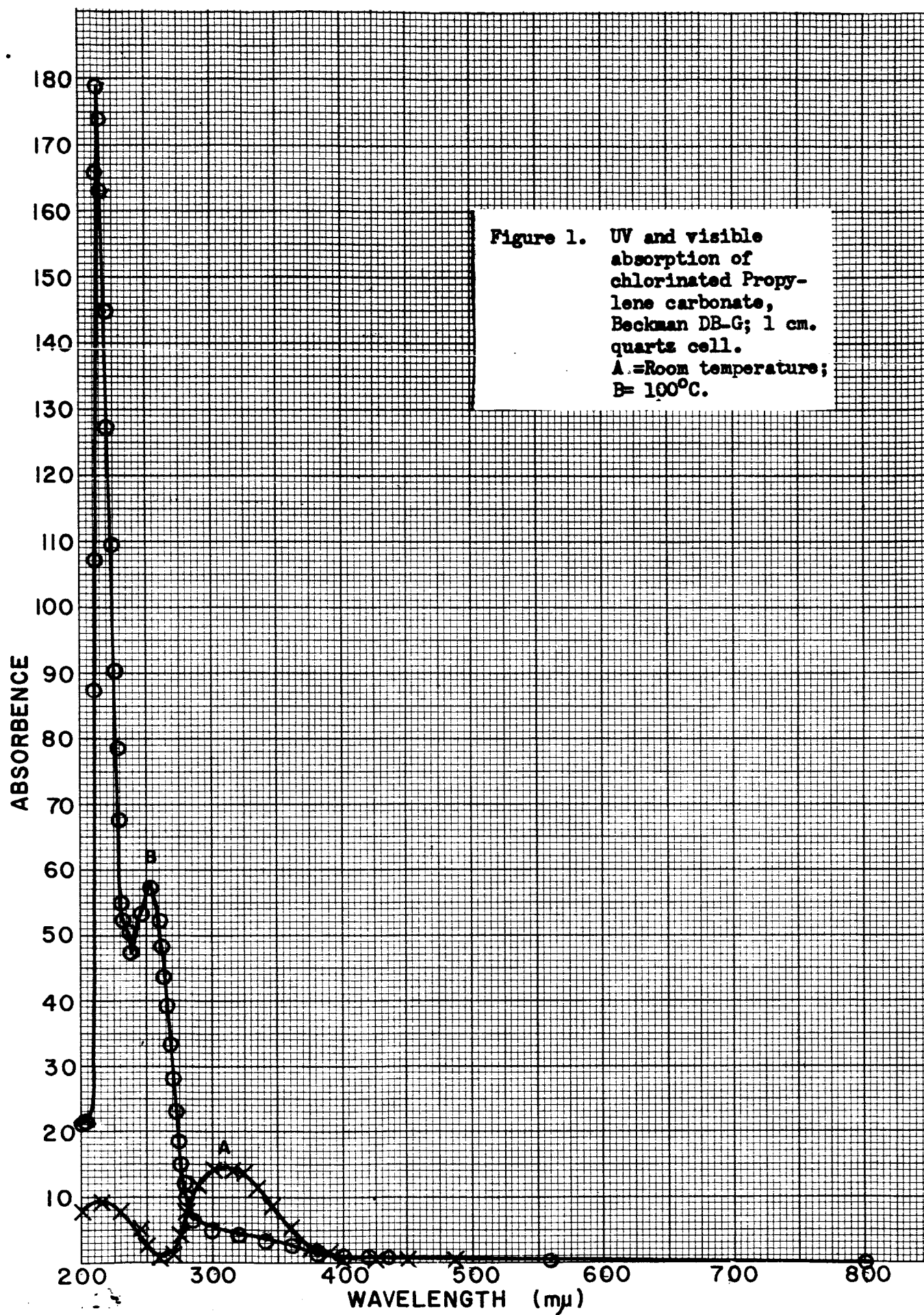
100 ml. volumes of redistilled butyrolactone were chlorinated at room temperature and at 100°C . Chlorine was bubbled through the solvent using a medium porosity gas diffusion tube for 2.5 hours. For the experiment at 100°C the flask holding the butyrolactone was held in an oil bath at that temperature. In both cases chlorine gas was dissolved in the solvent; a yellow color persisted for several hours. The refractive index of the liquid remained about the same, 1.4356 before and 1.4353 after the experiment. There was no change in the infrared curves or in the gas chromatograms. The color disappeared after standing for several hours.

The appearance of propylene carbonate after chlorination at 100°C suggested chemical change in the solvent. There was no change in the infrared spectra but the refractive index changed from 1.4203 to 1.4265 during the passage of chlorine gas. The

color of the solution changed, becoming orange with time. The absorption was measured in the UV and visible regions against unreacted propylene carbonate as a blank. Absorption was observed in the 200-300 m μ region as indicated by figure 1. Apparently the reaction is not very rapid. It appears that the chlorine gas dissolves in propylene carbonate and continues to react with time.

At room temperature a similar reaction occurred. The spectra of the solution ten days after chlorination is shown in figure 1. The absorption maximum occurred at 320 m μ as contrasted to the absorption peak at a lower wave length for the higher temperature chlorination.

These experiments are rather fragmentary and further study of this chlorination reaction is needed before significant conclusions can be drawn.



III. RANGE OF ELECTROLYSIS

A. General

The investigation of the range of electrolysis of the cyclic esters takes into consideration a number of related items that influence the electrochemical behavior of the solvents or influence the measurement of the electrochemical behavior. For example, methods of establishing the purity of the solvent, particularly with respect to oxidizable or reducible species, such as water, are important. The reactions of various metals with the electrolytic solutions must also be considered. The reactions with the alkali metals were discussed above. The whole question of what constitutes a suitable reference electrode has not been adequately answered in this field. These questions are considered in the following paragraphs.

B. Solvent Characterization

Various techniques have been used to establish solvent purity and to determine the presence of impurities. These include infrared absorption, gas chromatography, conductivity, refractive index, electrolysis, and titration with Karl Fischer reagent. Infrared spectra are very useful in establishing the presence of impurities in large concentration and the structure of unknowns or derivatives in reaction mixtures, and for these purposes are used continually. However, for the identification of compounds at low concentrations infrared absorption lacks the desired sensitivity. Very often

we are interested in a compound present in the ppm range.

The gas chromatograph has been extremely useful in establishing the purity of butyrolactone. An Anakro instrument has been used with a column material of diethylene glycol succinate. This instrument has a thermal conductivity detector and a helium carrier gas is used at a column flow rate of 54 cc. per minute. Samples of 15 to 50 μ l of butyrolactone are injected and the areas under the peaks mechanically integrated to estimate the composition of the mixture. The diethylene glycol succinate column is very satisfactory in separating butyrolactone from its impurities, most of which are lower boiling than the lactone. A typical chromatogram is given in figure 2. This chromatogram resulted from a 50 μ l injection of the first cut from a distillation of a sample of commercial γ -butyrolactone (Matheson, Coleman & Bell, #7042, BX2185). The peak resulting from low boiling impurities arises shortly after the air peak.

This column is also capable of separating water from butyrolactone but the sensitivity with this particular system is not sufficient to allow the use of the gas chromatograph for the quantitative determination of water in very low concentrations. Figure 3 is a typical curve showing definite separation of the water peak and the lactone peak. A series of solutions were prepared with known amounts of water up to 5% by volume. The areas beneath the curves were measured with a planimeter and plotted against the water content (figure 4). The indicated sensitivity is of the order of 0.1-0.2% water (1000-2000 ppm).

Figure 2. Gas chromatogram-
low boiling impurity
in γ -butyrolactone,
concentrated in
first distillation
cut.

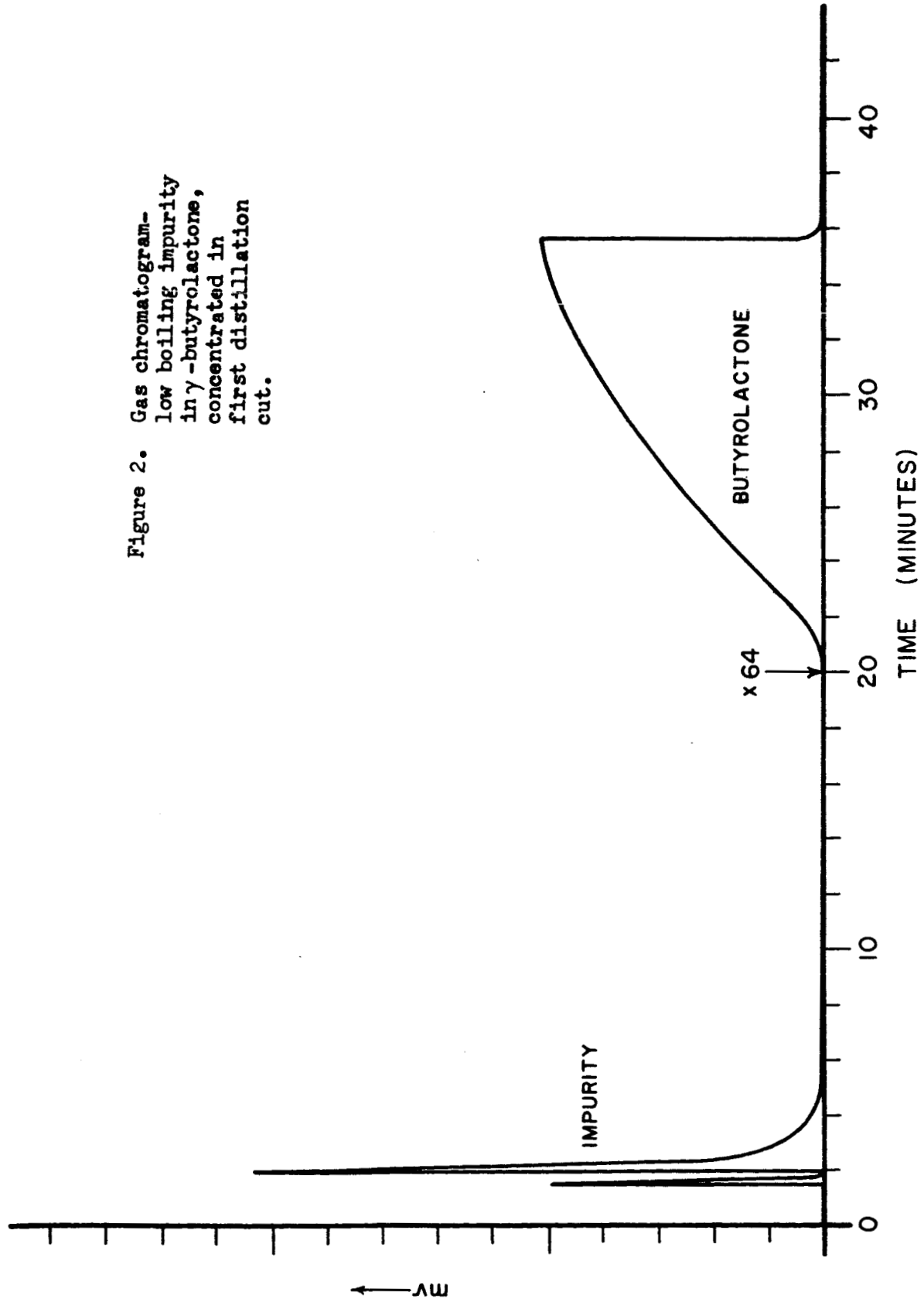
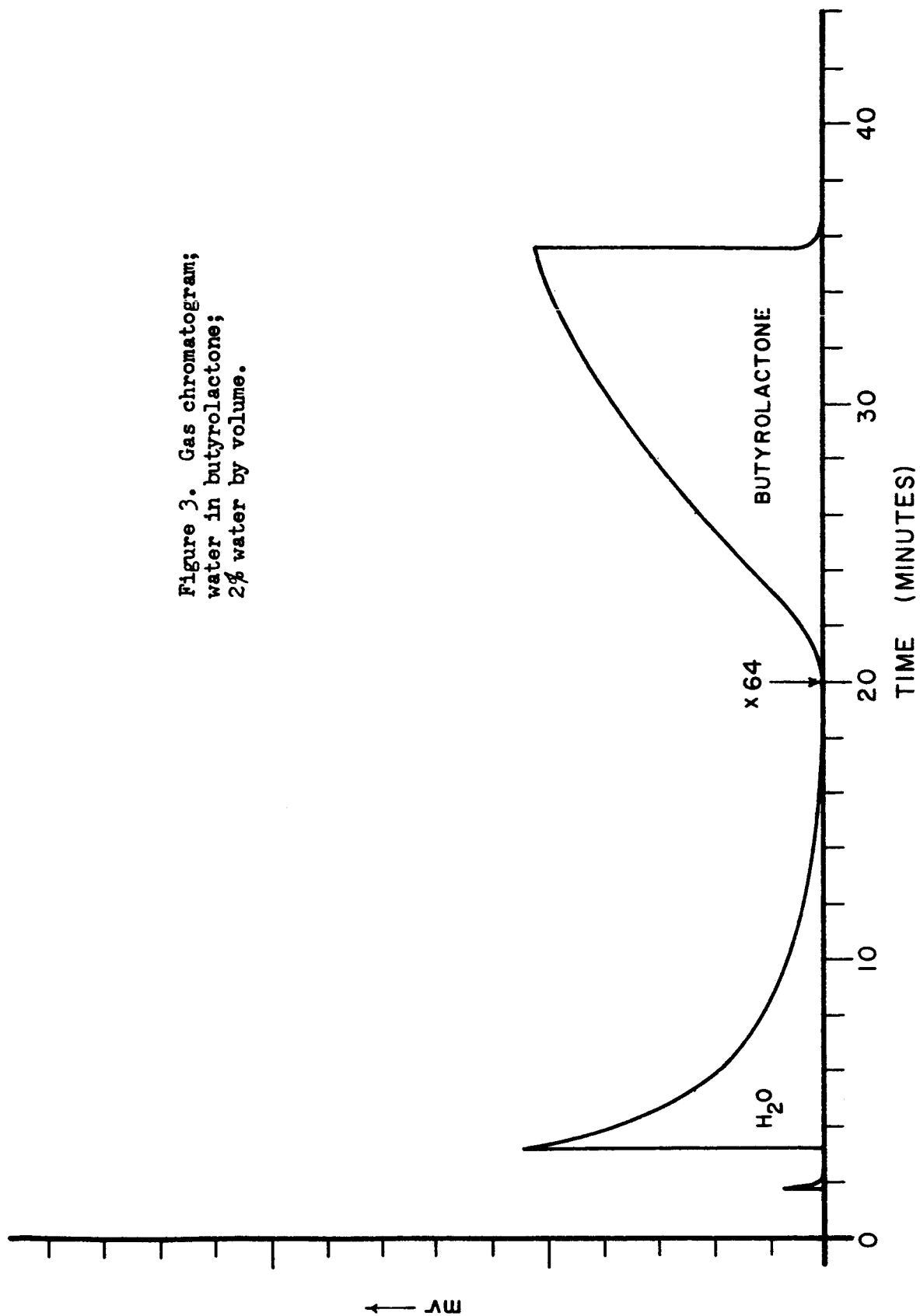
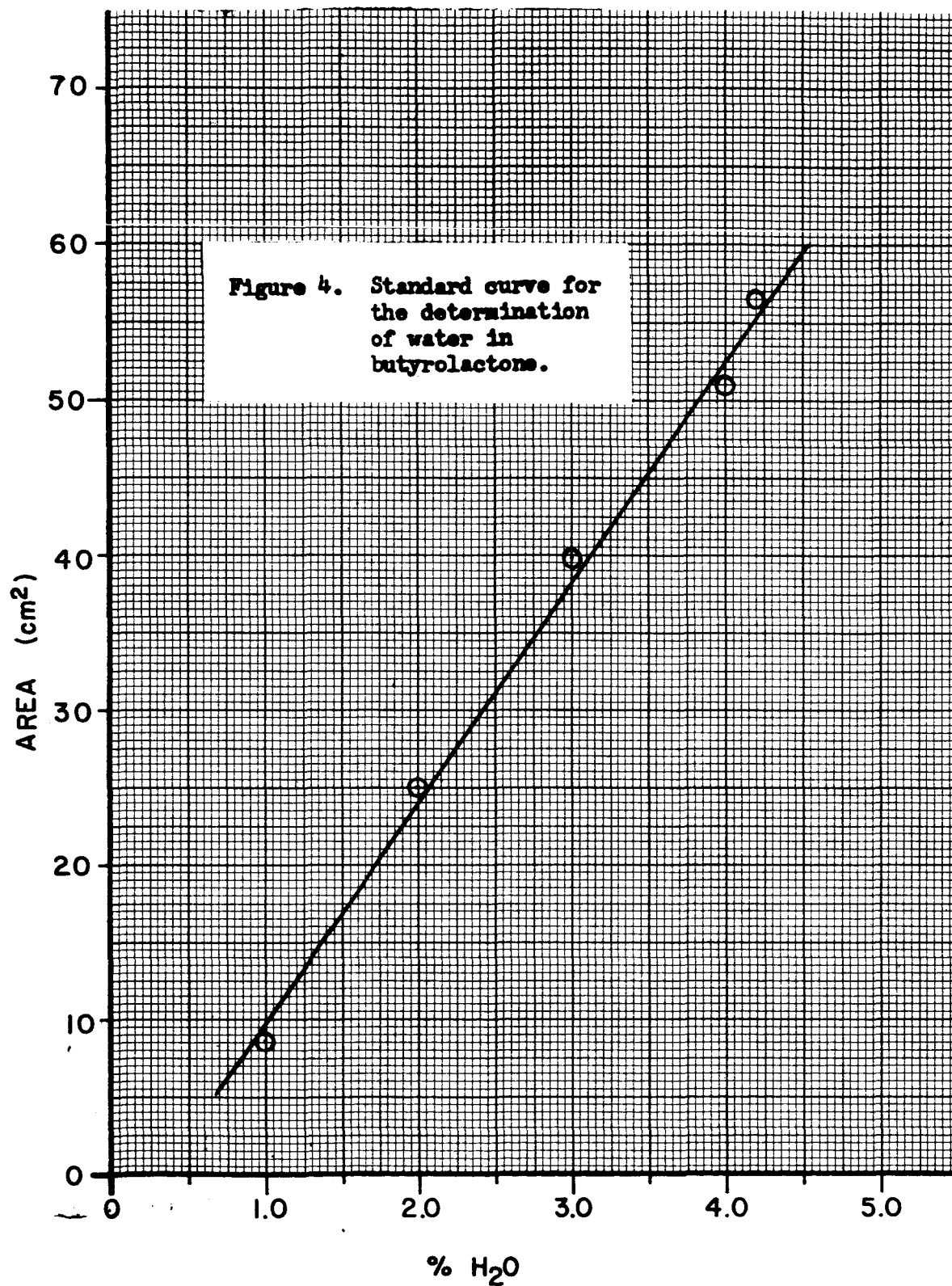


Figure 3. Gas chromatogram;
water in butyrolactone;
2% water by volume.

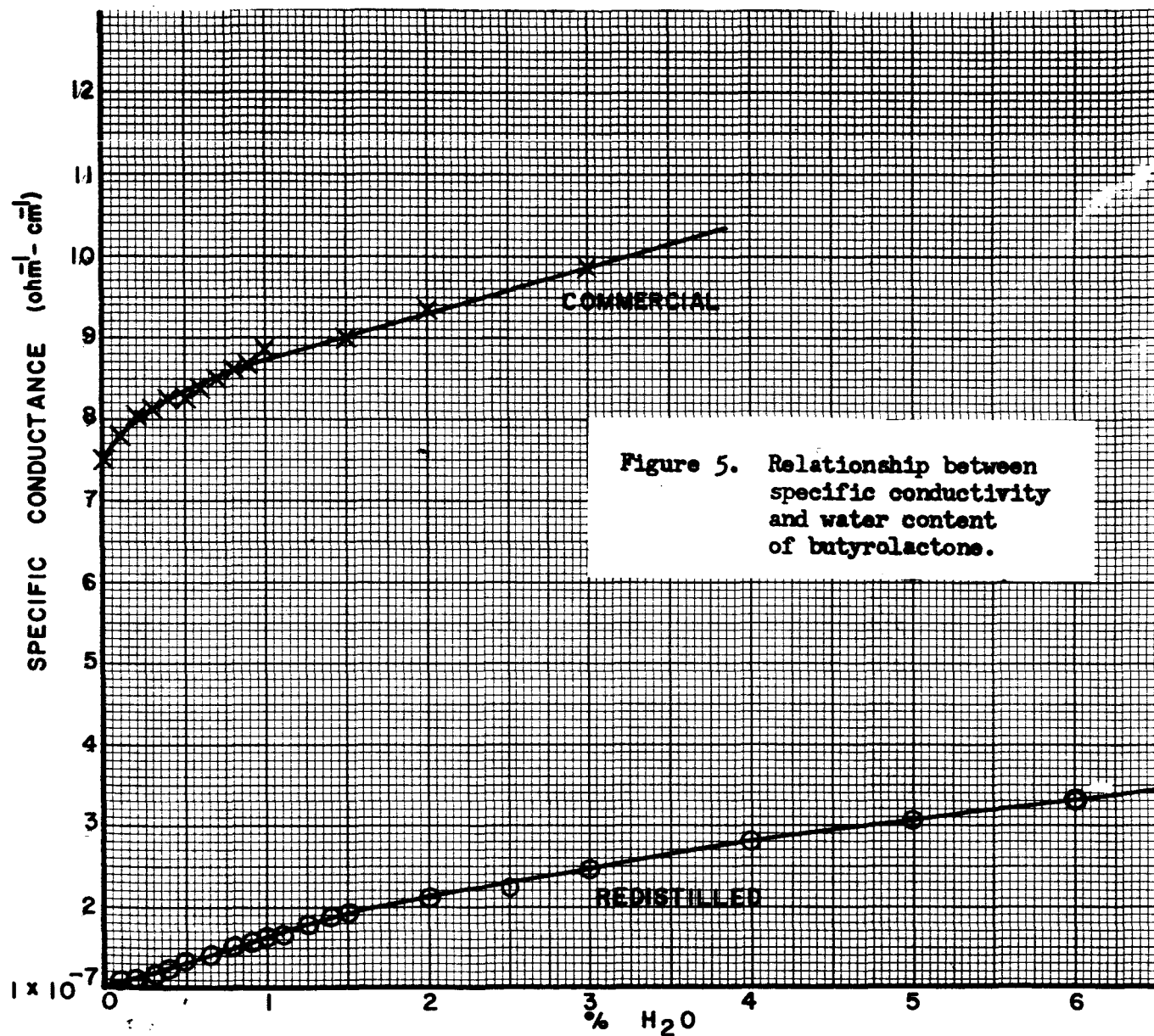


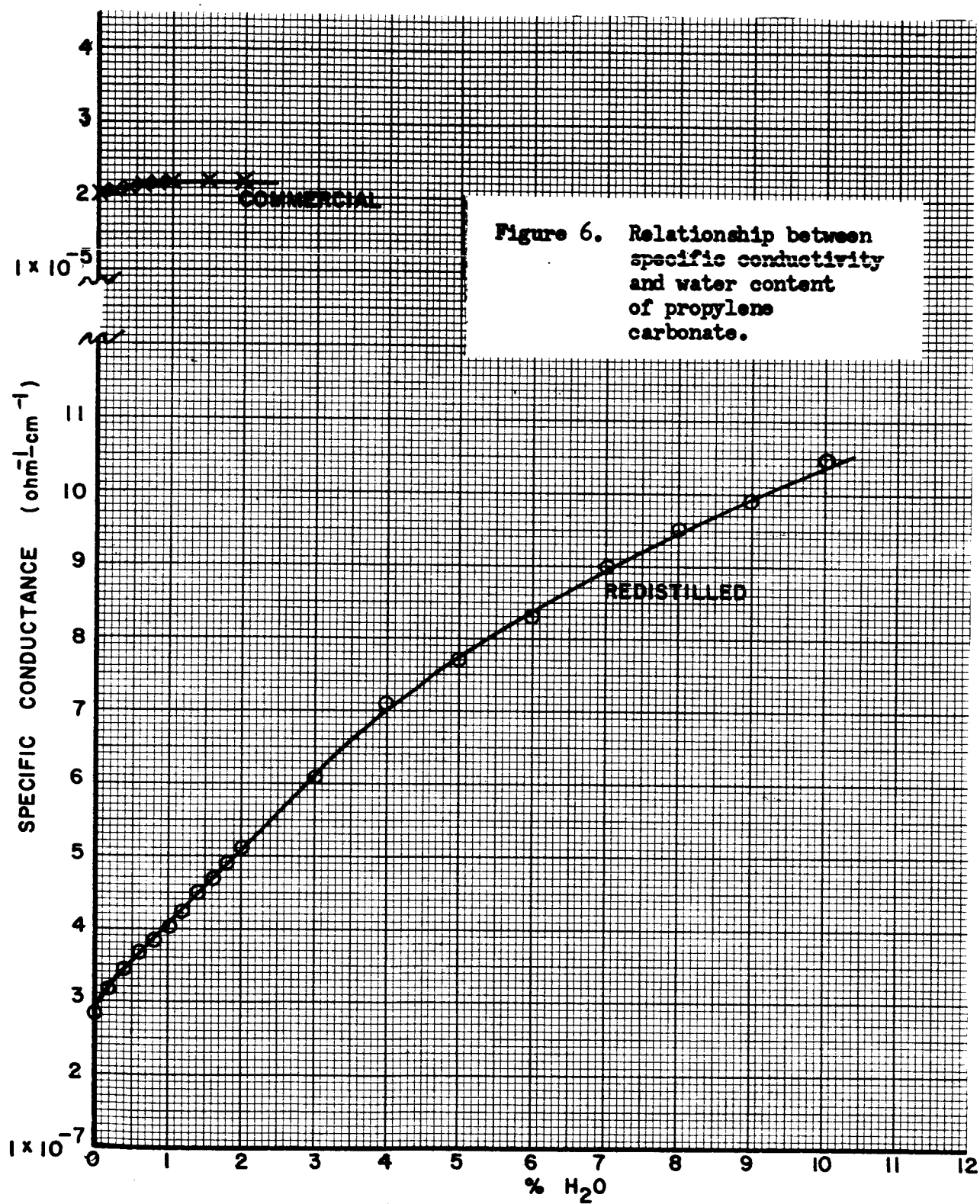


The gas chromatographic method is of significance because of its specificity and the small sample (25-50 μ l) required for the analysis. For this reason it would be desire to increase the sensitivity by using improved columns and improved detectors. The separation of gaseous mixtures, similar to water and lactones or propylene carbonate, using porous polyaromatic polymer beads has been reported by Hollis (8). A column composed of this material is available for installation in the present chromatograph to improve the sensitivity of the water determination.

Methods for the determination of water in butyrolactone based on electrical conductivity have about the same sensitivity, i.e. 0.1% H_2O in butyrolactone and propylene carbonate, as gas chromatography, but they are not specific for water. The specific conductivities of commercial butyrolactone and propylene carbonate are quite high and the range of conductivities is also considerable even when dealing with "white label" commercial material. Figures 5 and 6 show the change in specific conductivity of solutions of the two solvents with varying percentages of water. This measurement, of course, reflects all conducting species in the solution. An attempt to amplify this measurement was made by saturating samples of redistilled butyrolactone and redistilled butyrolactone containing 0.1% water with LiCl. It was expected that the enhancement of the solubility by traces of water would increase the conductivity. This was not the case as both solutions had approximately the same conductivity, which was $2.66 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.

One of the standard methods for the determination of water in organic solvents of this type is by titration with Karl Fischer





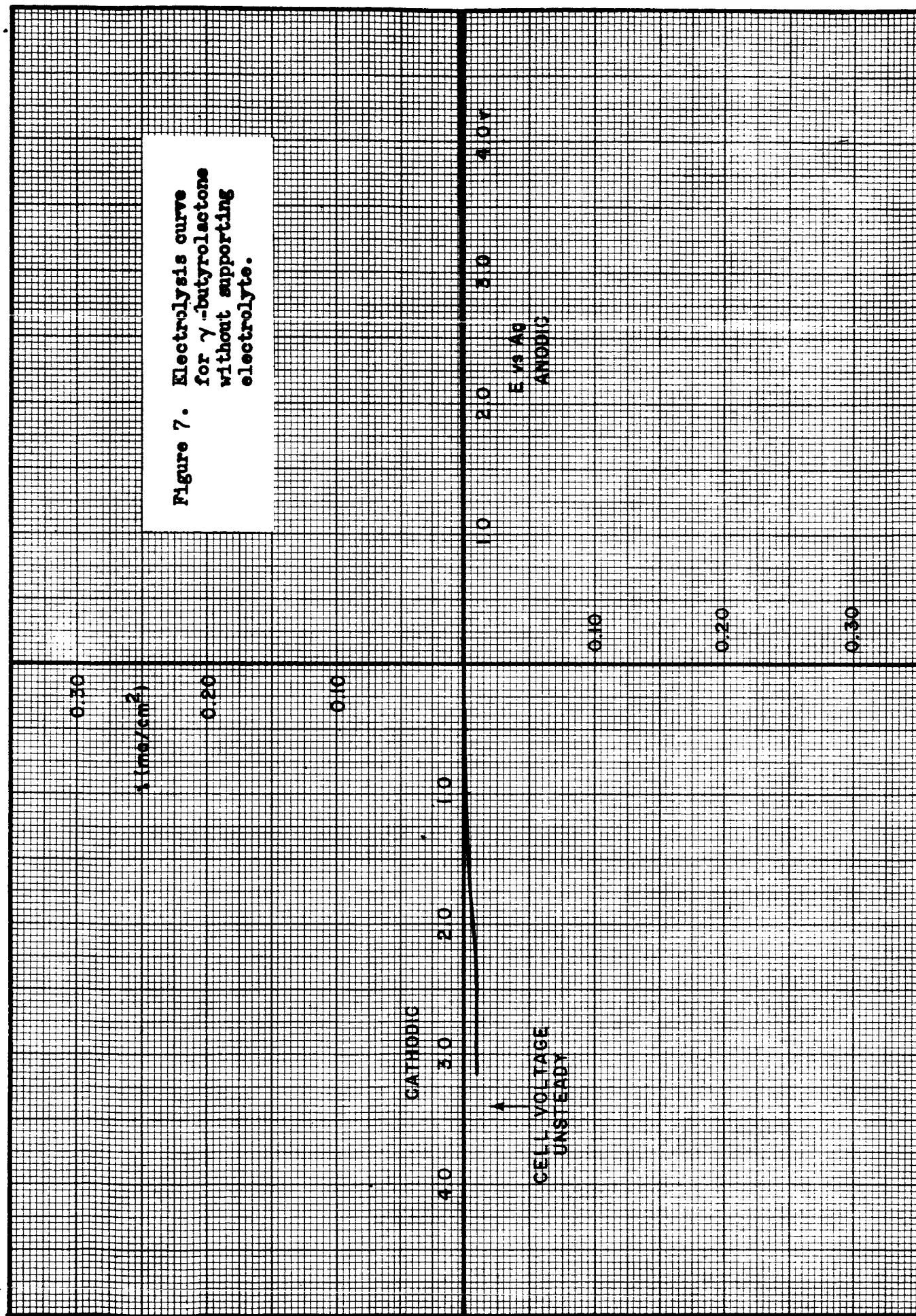
reagent. The reagent obtained from Fisher Scientific Co. was standardized with sodium tartrate dihydrate and also with a standard methanol solution containing 1 mg. H_2O per ml.

Butyrolactone as received from the manufacturer (Matheson, Coleman, and Bell), initially contained 101 ppm. H_2O . Propylene carbonate from the same source contained 1410 ppm.

Redistilled butyrolactone and propylene carbonate gave titration values no greater than the blank, which meant that the water content was 20 ppm or less. This material was used for the electrolysis experiments described in other sections.

The electrolysis of the solvent in the absence of a supporting electrolyte measures gross oxidizable and reducible compounds. In the absence of the supporting electrolyte, the "residual" current must be maintained by the transport of the electroactive species to the electrode. The residual current is low as seen by the plot in figure 7 of an electrolysis curve for butyrolactone.

To maintain the anode at a potential of 5.0 volts and a cell current of 0.05 ma, a cell voltage of 6.4 v. was required. At a cathode potential of 3.0 volts a cell voltage of 9-10 v. was required to maintain a cell current of 0.1 ma. The particular solvent used in this experiment had been distilled at 10.25 mm-10.5 mm. and 85.50-84.78°C, and then held over type 4A molecular sieves for 6 months. Commercial butyrolactone (Matheson, Coleman, and Bell, #7042) which contains about 101 ppm of H_2O gave a very similar type of electrolysis behavior.



C. Reference Electrode

In the field of non-aqueous electrochemistry there have been a number of attempts made towards establishing a suitable reference electrode. The first has been the employment of an aqueous reference such as a saturated calomel half-cell connected to the working cell by a salt bridge (9). This would appear to be highly undesirable because of a large and unknown junction potential and the possibility of introducing water into the solution. The second has involved a metal-insoluble salt of the metal, such as Ag-AgCl in equilibrium with chloride ions (10). This electrode has been successfully employed in systems that contain the reversible species in the electrolyte, e.g. aluminum chloride solutions. Another approach has involved a similar system (Ag-AgBr) connected electrically to the working cell by means of a salt bridge (11). The fourth type is the metal-metal ion electrode positioned in the electrolyte close to the working electrode (5). The final type is the metal-metal ion type connected to the electrolyte through a salt bridge and separated by a glass frit (12).

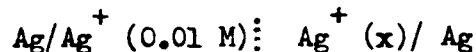
The main requirements for a suitable reference electrode are reproducibility and constancy. Whereas, reversibility is desirable and adherence to the Nernst equation is informative with respect to transference characteristics it is not essential in view of the use of high impedance electrometers in which the current passing on measurement is 10^{-12} - 10^{-14} amp. (i.e. at a current density much lower than exchange current densities due to oxidation or reduction of impurities in solution).

As a basis for developing a reliable reference, the stability of silver in certain electrolytic solutions was investigated. For these experiments silver wire of 10 cm² area was immersed in 50 ml. of an electrolytic solution at room temperature for times up to three months. In a 0.86M solution of LiClO₄ in redistilled butyrolactone a weight change of -0.3 mg (average) was observed. In a 0.336 M solution of recrystallized KPF₆ in commercial propylene carbonate an average weight change of +0.2 mg was observed. These values approximate experimental error and it was concluded that the chemical dissolution or corrosion of silver in these two typical electrolytic solutions was negligible.

Silver will dissolve anodically in LiClO₄ solutions in butyrolactone and propylene carbonate at a rate predicted by Faraday's law. Experiments were conducted in an H-type cell in which the anode and cathode compartments were separated by a fritted glass disc. The anodically dissolved silver remains in the anode compartment and precipitates as a reddish-brown salt when solubility is exceeded. During the electrolysis Li was deposited at the platinum cathode at a high efficiency, i.e. 2.31 mg. of Li expected and 2.07 mg determined by titration in aqueous solution with standard acid.

In a similar type of H-cell, fitted with a Teflon stopcock, the emf of solutions of silver nitrate of several dilutions were measured. Measurements made with a concentration cell type of arrangement determines agreement or disagreement with the type of behavior expected from the Nernst equation. A 0.01M solution of

AgNO_3 (Fisher's Certified Reagent) in γ -butyrolactone was prepared and solutions 0.001 M, 0.0001 M, and 0.00001 M were prepared by dilution. Concentration cells of the type



were assembled in which "x" was successively, 0.01M, 0.001M, 0.0001M, and 0.00001M. The potentials of these cells were measured with a Radiometer pH Meter 22 with a Type PHA630P Scale Expander.

For the four concentrations of x, the following potentials were observed.

<u>x</u>	<u>E (mv)(average)</u>	<u>Δ</u>
0.01M	+0.5	0
0.001M	-48.7	(49.2) 1
0.0001M	-92.4	(46.5) 2
0.00001M	-145.2	(48.6) 3

The average emf for the cell with the 10 fold dilution was 48 mv. This arrangement is a concentration cell with transference and the emf is given by

$$E = 2t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$$

where a_2 and a_1 are the appropriate activities, and t_- is the transference number of the nitrate ion. For the cell at 25°C and an activity ratio of 10

$$E = 2t_- (0.059)$$

For the case above $t_- = 0.41$. The implication of this will be discussed below.

The drift of the silver reference electrode over extended periods of time has been of concern. Several experiments were performed

in which the potential of the silver wire reference was measured against one of the large platinum electrolysis electrodes.

Typical behavior is shown in figure 8. There is a fairly rapid change in potential within the first hour followed by a plateau followed by a further decrease in potential. The plateau accounts for the consistency observed in the electrolysis experiments reported previously. The reason for the drift can not be explained at this point other than to say that it is unlikely that solubility of Ag in this electrolyte is the cause.

To achieve greater stability for the reference measurement, an auxiliary reference electrode was placed in the system. This electrode was connected to the electrolysis solution through a fritted-glass-terminated side arm. The side arm held a silver wire electrode immersed in 0.01M AgNO_3 solution. The new cell design is shown in figure 9. The potential of the silver wire reference located between the large platinum electrolysis electrodes was compared with the Ag/Ag^+ reference in the side arm. This comparison is shown in figure 10. The platinum electrode is negative to the Ag/Ag^+ electrode and the measurement is constant within about 10 mv. over several days. The platinum electrode is positive to the Ag wire located adjacent to it and drifts over the same period of time.

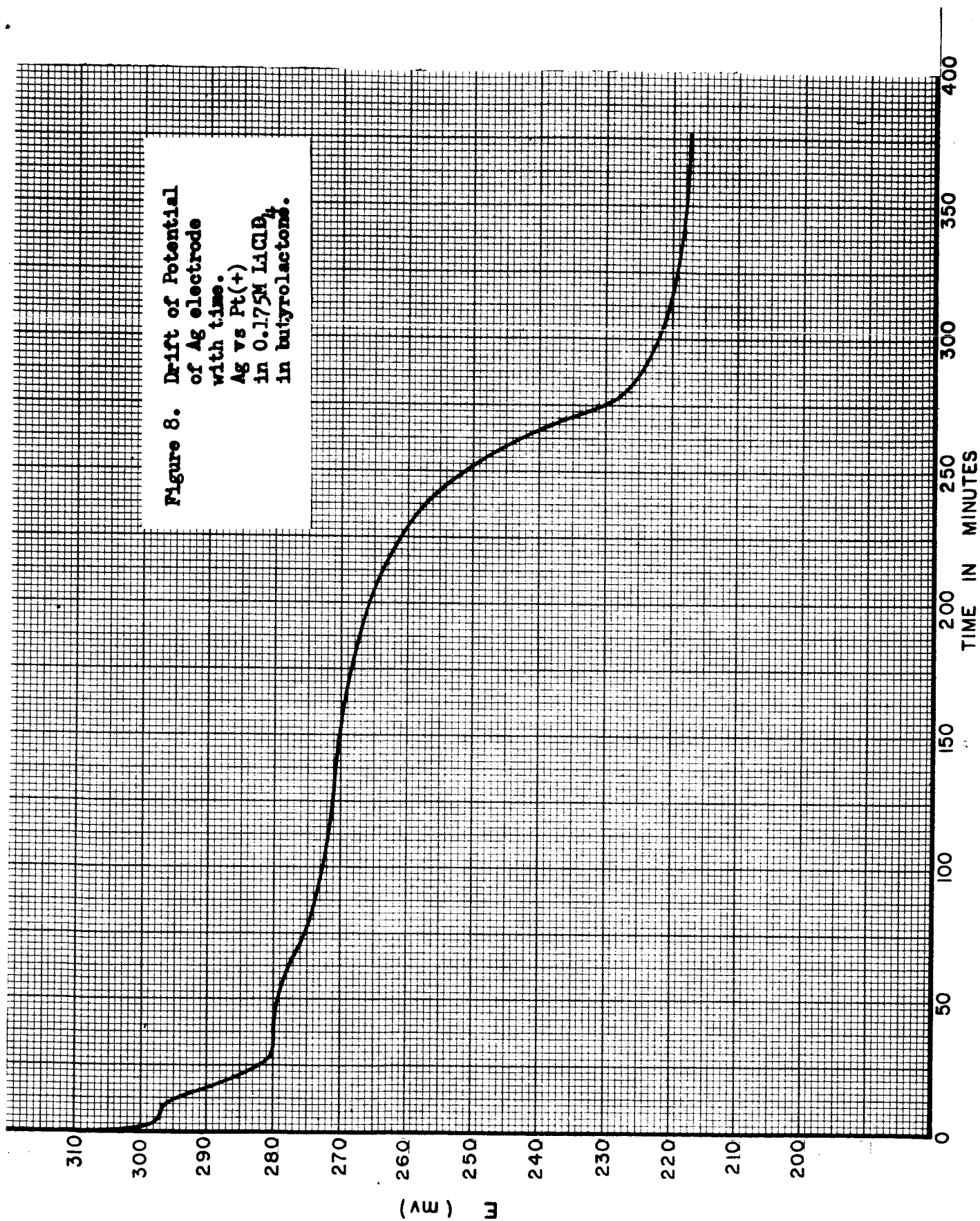
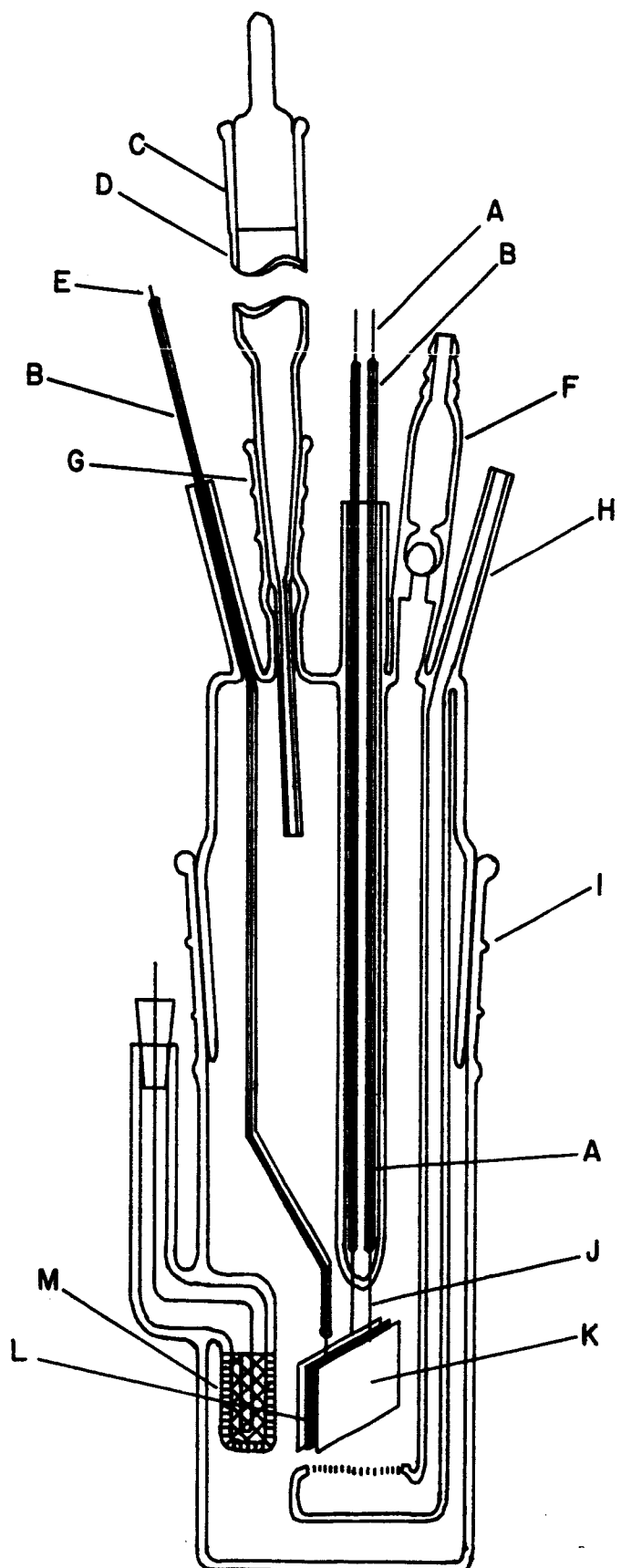


Figure 9 ELECTROLYSIS CELL



A - Electrode lead (Copper)

B - Teflon sheath

C - Standard taper joint,
14/35

D - Filling tube

E - Silver wire
reference electrode

F - Check valve

G - Standard taper joint 10/30

H - Gas diffuser tube

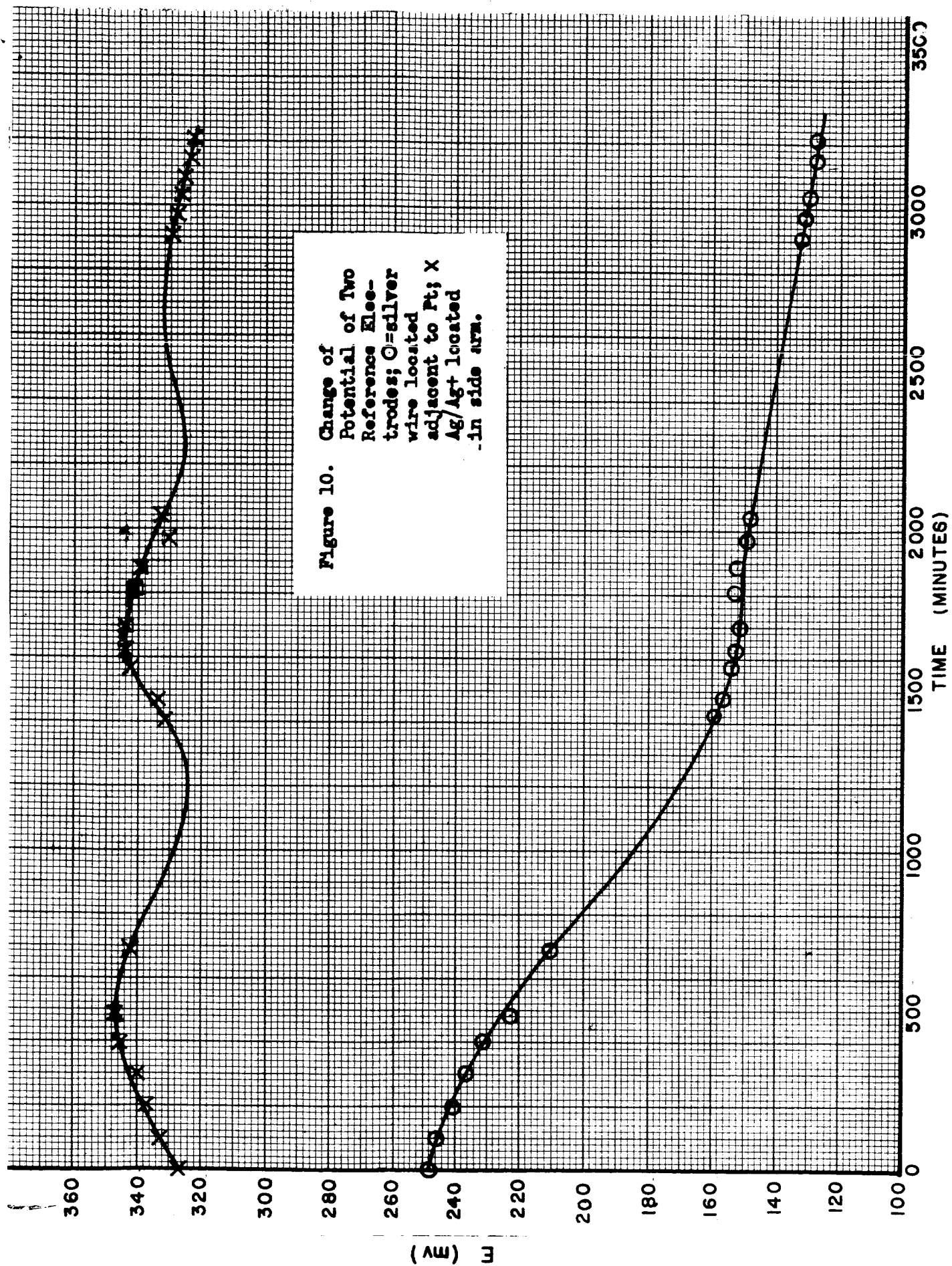
I - Standard taper joint,
55/50

J - Electrode lead
(platinum)

K - Electrode (platinum)

L - Separator
(glass fiber paper)

M - Ag/Ag⁺ reference



IV. CONCLUSIONS AND DIRECTION OF FUTURE EFFORT

The experimental results, as well as reports published in the literature, indicate that a Ag/Ag^+ electrode, separated from the electrolysis compartment by a salt bridge, is the most suitable reference for this non-aqueous work. The separation is required for experimental reasons in this investigation. Ag^+ ions can not be tolerated in the solution during the electrolysis process. For a similar reason, interference from halide ions, reference electrodes such as Ag/AgCl are not suitable. For these systems the more desirable anion for the reference half-cell is the perchlorate ion. It would be expected that this would tend to minimize junction potential differences.

With regard to future effort it is intended to complete the range of electrolysis work described in the two previous reports using the Ag/Ag^+ reference electrode.

The concentration cell experiments indicated that the transference number for Ag^+ in AgNO_3 solutions in butyrolactone is 0.59. The accepted value for the cation transference number in aqueous solutions of silver nitrate is 0.46(13). It is concluded that the transport characteristics for these ions in butyrolactone are very different from those in aqueous solution, with the cation rather than the anion carrying the greater part of the current. The utilization of this experimental technique should give a great deal of information regarding transport properties of electrolytes and also the solvation characteristics of ions.

The study of the reactions of the cyclic esters with the alkali metals and with chlorine has shown the possibility of certain reactions which could be quite significant in the operation of galvanic cells. Notable among these are the ring opening and condensation characteristics of Na and the tendency for Cl_2 to react over a long period of time with propylene carbonate to form a new chlorinated species. Whereas, there are several questions left unanswered with regard to the identification of certain species involved in the reactions it is felt that at this point it is sufficient to describe the mechanism in a general way as outlined in Section IIIA. It would be desirable to learn more about the reaction of halogens and the cyclic esters, however. It is intended to pursue this point in our future work.

There appear to be several reliable methods for characterizing these cyclic esters and establishing impurity content. Of these, gas chromatography has been quite successful. It is expected that greater sensitivity for the determination of water will be achieved with an improved column and it is intended to establish this method for routine water determination.

V. REFERENCES

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